Sterically hindered tetrylenes based on new 1,10-phenanthroline-containing diols: initiators for ε-caprolactone polymerization*

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Previously unknown tetradentate ONNO-type ligands **1—5** (4,7-di(4-R′-phenoxy)-2,9-di(HOCR$_2$CH)-1,10-phenanthrolines (R′ = Me, R—R = —(CH$_2$)$_5$— (**1**), R = Me (**2**), R—R = 2,2-adamantylene (**3**); R′ = Bu^t, R—R = —(CH$_2$)$_5$— (**4**), R = Me (**5**)) were synthesized by sequential treatment of 2,9-dimethyl-4,7-di(4-R′-phenoxy)-1,10-phenanthrolines **6** (R′ = Me) and **7** (R′ = Bu^t) with excess LDA and appropriate dialkyl ketone. The structure of compound **4** was determined by single-crystal X-ray diffraction. Previously uncharacterized phenanthroline **6** was synthesized by the treatment of 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline with excess *p*-cresol in the presence of KOH. The reaction of compounds **1—5** with one equivalent of Lappert′s germylene or stannylene, M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn), gave the corresponding germylenes **8—12** (M = Ge, R′ = Me, R—R = —(CH$_2$)$_5$— (**8**), R = Me (**9**), R—R = 2,2-adamantylene (**10**), R′ = Bu^t, R$_2$ = —(CH$_2$)$_5$— (**11**), R = Me (**12**)) and stannylenes **13—17** (M = Sn, R′ = Me, R—R = —(CH$_2$)$_5$— (**13**), R = Me (**14**), R—R = 2,2-adamantylene (**15**), R′ = Bu^t, R—R = —(CH$_2$)$_5$— (**16**), R$_2$ = Me (**17**)) in satisfactory yields. According to ^{1}H, ^{13}C, and ^{119}Sn NMR data, the synthesized stannylenes are monomeric in solution, and the tin atom has a coordination number of 4. In the series of the compounds under consideration, stannylene **16** proved to be the most active initiator for ε-caprolactone polymerization, whereas the germylenes were shown to be inactive in this process.

Key words: germanium, tin, germylenes, stannylenes, tetrylenes, ring-opening polymerization, poly-ε-caprolactone.

Past decades have witnessed the ever-increasing use of biodegradable polymers.[1,2] These compounds, having physicomechanical properties similar to those of classical α-olefin-based polymers, easily degrade in nature. The half-life of biodegradable polymers in soil is usually no longer than one-to-two years. The application of these materials instead of classical α-olefin-based polymers helps address issues associated with environmental pollution. It is important that most biodegradable polymers can be produced from biomass and, besides, they are often bioresorbable.

The polymerization of cyclic esters (lactide, glycolide, ε-caprolactone) using transition and main-group metal complexes as initiators is most commonly applied to synthesize such polymers (most of which are hydroxycarboxylic acid derivatives).[3—9] Increasing efforts are being made to develop new initiators for ring-opening poly-

merization with improved characteristics. The design of new catalytic systems containing electron-deficient metals is primarily based on the synthesis of new ligands. The ligand environment is responsible for Lewis acidity and steric accessibility, which has a crucial influence on the properties of the initiator. Therefore, the development of new ligand systems, the synthesis of new catalysts based on these systems, and the elucidation of the structure—catalytic property relationship for the complexes are challenging problems.

The goal of this work is to synthesize new tetrylenes based on previously unknown alkyl-substituted diols of the phenanthroline series and study their behavior as initiators for ε-caprolactone polymerization.

Results and Discussion

Previously, we[10—18] and other authors[19—24] showed that dianions of diols (diphenols) containing one or two

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* Dedicated to Corresponding Member of the Russian Academy of Sciences G. I. Nikishin on the occasion of his 90th birthday.

nitrogen atoms, which are capable of being involved in additional transannular interaction with the germanium or tin atom, are very efficient ligands stabilizing compounds of heavy Group 14 elements in oxidation state 2+. Previously, we have synthesized 4,7-di(4-*tert*-butylphenoxy)-2,9-di(2-hydroxy-2,2-diphenylethyl)-1,10-phenanthroline as one of such ligands.[10] Stannylene based on this ligand proved to be a highly active initiator for ε-caprolactone polymerization.[10] In order to extend the range of families of such ligands and, correspondingly, tetrylenes based on these ligands and to elucidate the influence of the nature of substituents on the polymerization activity of the initiator, we synthesized new ligands **1—5** containing alkyl groups R in substituents CH₂CR₂OH (Scheme 1).
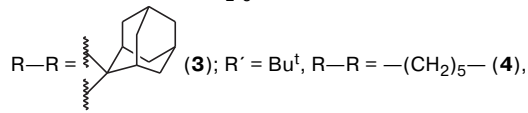
Compounds **1—5** were synthesized using a procedure developed in our previous study.[10] The starting 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline and 2,9-dimethylphenanthroline (**7**) containing 4-*tert*-butylphenoxy groups in positions 4 and 7 were prepared according to a known procedure.[10] The reaction of 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline with 2 equiv. of the 4-methylphenoxide anion under drastic conditions leads to the replacement of chlorine atoms by phenoxy groups to give the corresponding phenanthroline **6** in high yield. The reaction of compounds **6** and **7** with 3 equiv. of LDA followed by the treatment of the generated dilithium salts with excess of the appropriate dialkyl ketone gave diols **1—5** in satisfactory yields. The structure of diol **4** was determined by X-ray diffraction (Fig. 1). To the best of our knowledge, this is the first X-ray structure of diols of the 1,10-phenanthroline series. In the crystal of diol **4**, there are two strong intramolecular O—H...N hydrogen bonds, whereas intermolecular O...H—O hydrogen bonds are absent. A similar binding mode was found in related diols of the pyridine series 2,6-di(HO—A—CH₂)₂C₃H₃N (A = CPh₂, C(4-FC₆H₄)₂).[25,26] By contrast, both strong intramolecular O—H...N hydrogen bonds and intermolecular O...H—O hydrogen bonds were found in adamantylene diol 2,6-di(OH—A—CH₂)₂C₃H₃N (A is 2,2-adamantylene).[27]

The alkoxydeamination of Lappert's germylene or stannylene M[N(SiMe₃)₂]₂ (M = Ge, Sn) with ligands **1—5** gave tetrylenes **8—12** (M = Ge) and **13—17** (M = Sn) in satisfactory yields (Scheme 2).

The structures of all the new compounds were confirmed by NMR spectroscopy and elemental analysis. According to ¹H and ¹³C NMR data, tetrylenes **8—17** are symmetrical, with both oxaalkyl groups and both nitrogen-containing six-membered aromatic rings being equivalent in each compound. Unfortunately, we failed to grow crystals of tetrylenes suitable for X-ray diffraction, but we studied the structures of stannylenes **15—17** in solution by ¹¹⁹Sn NMR spectroscopy. The signal of the tin atom of these compounds is in the range from δ −365 to −320 (C₆D₆). In our previous study,[10] we analyzed the chemical

Scheme 1

6 (83%)

6, 7

1 (50%), **2** (45%), **3** (47%),
4 (49%), **5** (40%),
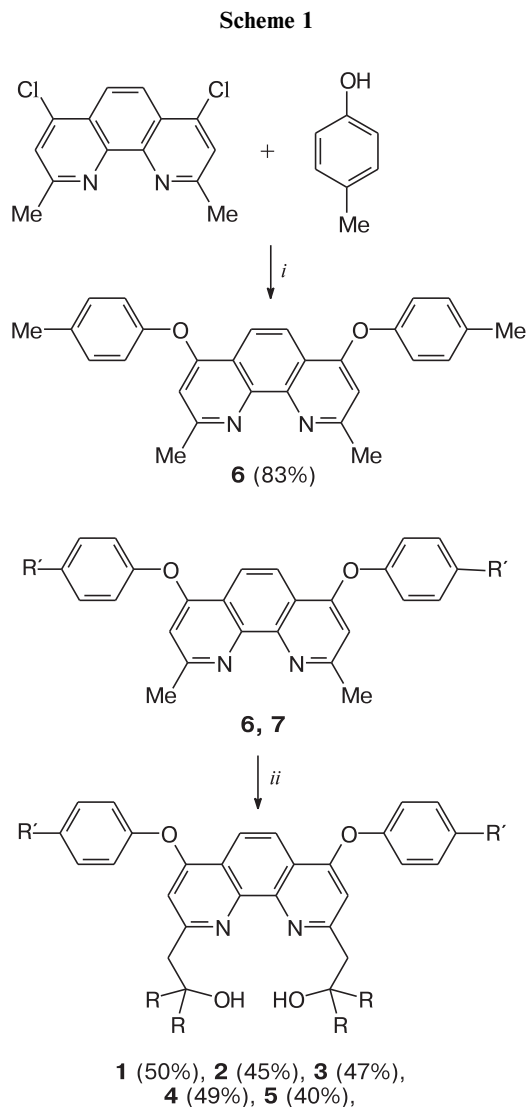
1—5: R′ = Me, R—R = —(CH₂)₅— (**1**), R = Me (**2**),

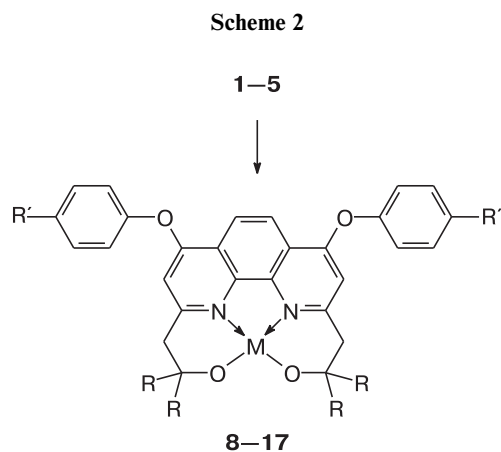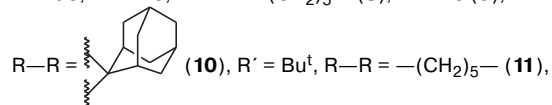R—R = (**3**); R′ = Buᵗ, R—R = —(CH₂)₅— (**4**),

R = Me (**5**),
6, 7: R′ = Me (**6**), Buᵗ (**7**)

Reagents and conditions: *i.* KOH, 130 °C; *ii.* 1) LDA, THF, −80 °C, 2) R₂CO, THF, −20 °C, 3) NH₄Cl, H₂O.

shifts of related compounds in detail. The chemical shift of the three-coordinate tin(2+) atom in the NO̲O environment (one oxygen atom forms a coordination bond with Sn) is in the range from δ −38 to −41 (in C₆D₅CD₃) for (Me₃Si)₂N(PrⁱO-μ)Sn, (Me₂N)(PrⁱO-μ)Sn, and (Me₂N)-(Ph₃SiO-μ)Sn.[28] By contrast, the chemical shift of the tin atom in the compound MeN[CH(*S*-Me)CH(*R*-Ph)O]-(CH₂CPh₂O)Sn (in C₆D₆) is δ −254.[29] In the cited study, the coordination number (CN) of the tin atom was not

Scheme 2

1—5

↓

8—17

8—17: M = Ge, R′ = Me, R—R = —(CH₂)₅— (**8**), R = Me (**9**),

R—R = ξ [adamantylidene] ξ (**10**), R′ = Bu^t, R—R = —(CH₂)₅— (**11**),

R = Me (**12**); M = Sn, R′ = Me, R—R = —(CH₂)₅— (**13**),

R = Me (**14**), R—R = ξ [adamantylidene] ξ (**15**),
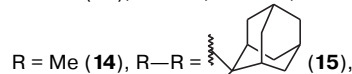
R′ = Bu^t, R—R = —(CH₂)₅— (**16**),
R = Me (**17**)

Compound	Yield (%)	Compound	Yield (%)
8	62	**13**	51
9	50	**14**	52
10	65	**15**	51
11	60	**16**	50
12	50	**17**	60

Reagents and conditions: M[N(SiMe₃)₂]₂ (M = Ge, Sn), toluene.

unambiguously determined (CN(Sn) = 3 or 4), and its was not established whether this complex is monomeric or dimeric and whether the ligand environment is O<u>N</u>O (one oxygen atom forms a coordination bond with Sn) or O<u>ON</u>O (one oxygen atom and one nitrogen atom form coordination bonds with Sn). Besides, the following chemical shifts of the tin atom were reported: δ −303 for dimeric stannylene [MeN(CH₂CH₂O)₂Sn]₂ (CN = 4, O<u>ON</u>O environment, one oxygen atom and one nitrogen atom form coordination bonds with Sn, in CD₂Cl₂),[30] δ −363 for [MeN(CH₂CH₂O)(CH₂CH₂NSO₂-*p*-Tol)Sn]₂ (CN = 4, O<u>NO</u>N environment, one oxygen atom and one nitrogen atom form coordination bonds with Sn, in CDCl₃),[17] and δ 423 for monomeric stannylene **18** (CN = 3, O<u>N</u>O environment, one nitrogen atom forms a coordination bond with Sn, in C₆D₆). In the latter case, high acidity of phenoxide oxygen atoms leads to an increase in the effective positive charge on the tin atom, which, in turn, causes an upfield shift of the signal of the tin atom despite CN(Sn) = 3.[18] For related monomeric stannylene **19** (CN = 4, O<u>NN</u>O environment, two nitrogen atoms form weak coordination

bonds with Sn), the chemical shift of the tin atom is δ −448 (C₆D₆).[10] The chemical shifts of the tin atom in C₆D₆ for dimeric stannylene **20** (CN = 4, O<u>ON</u>O environment, one oxygen atom and one nitrogen atom form coordination bonds with Sn)[11] and monomeric stannylene **21** (CN = 4, O<u>NN</u>O environment, two nitrogen atoms form coordination bonds with Sn)[18] are δ −486 and −514, respectively. Therefore, it can be concluded that compounds **15—17** in a solution in C₆D₆ are monomeric, and there are two Sn←N coordination bonds in their molecules; however, these bonds are apparently weak, as in stannylene **19**.

18

19

20

21
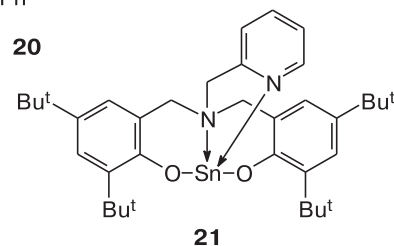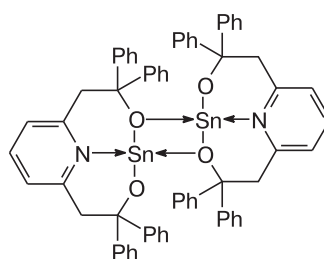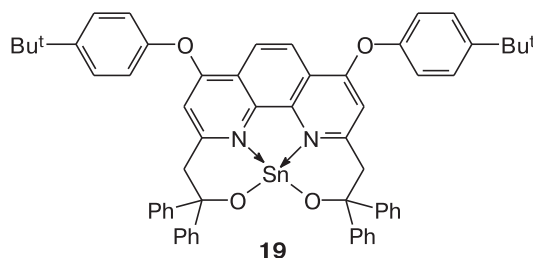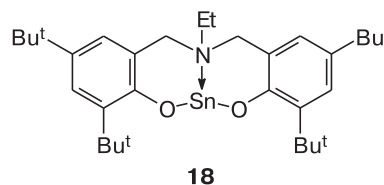
Germylenes **8—10** and stannylenes **15—17** were tested as initiators for ε-caprolactone polymerization. The reaction was performed in bulk in the presence of an external nucleophile (benzyl alcohol) at high temperature (conditions most commonly used in industry). The stannylenes under consideration were shown to be active initiators for ε-caprolactone polymerization (Table 1). In three runs, the conversion was almost 100% over 12 h. The values of the polydispersity index (Mw/Mn) were not higher than 1.6, which indicates that the polymerization is controlled (see Table 1, runs *7*, *11*, and *15*). By contrast, germylenes **8—10** are virtually inactive under these conditions (see
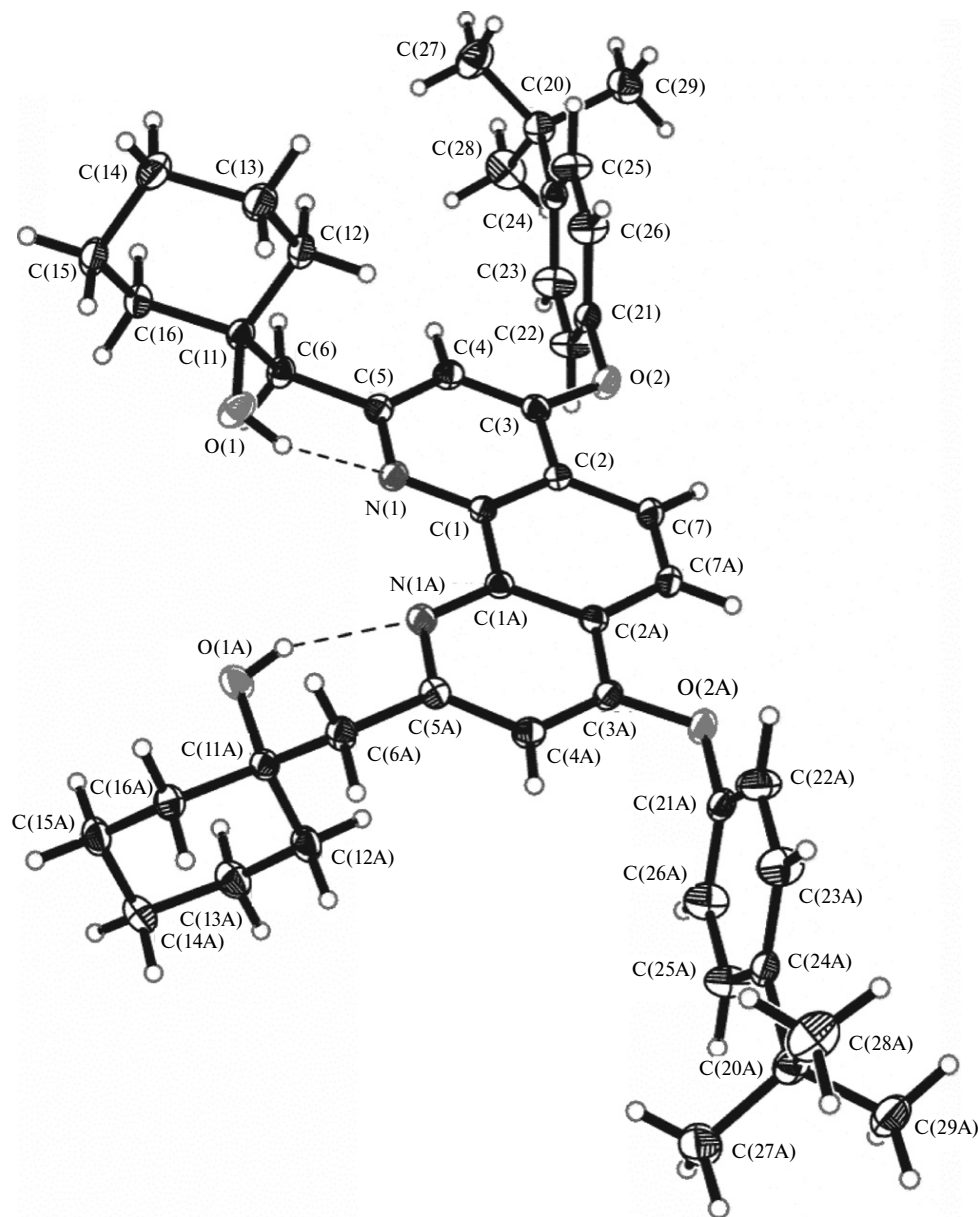
Fig. 1. Molecular structure of compound **4**. The chloroform solvent molecule is not shown. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (d/Å) and bond angles (ω/deg): d(O(1)—H(1)), 0.81(2); d(N(1)···H(1)), 2.00; d(O(1)—C(11)), 1.4386(16); d(O(2)—C(3)), 1.3644(16); ω(C(11)—O(1)—H(1)), 107.3(14).

runs *1—3*). It should be emphasized that the related germylene studied previously, which is structurally similar to stannylene **19** and which differs from compound **12** only in that it contains phenyl moieties instead of methyl groups in each oxoalkyl chain, proved to be a highly efficient initiator for ε-caprolactone polymerization (under similar conditions, the conversion was 98% over 12 h).[10] Consequently, it can be suggested that the replacement of phenyl substituents by alkyl groups causes a significant decrease in the Lewis acidity at the germanium site of germylenes.

To conclude, we synthesized five new ONNO-type ligands and ten new tetrylenes based on these ligands. The new stannylenes were shown to be efficient initiators for ε-caprolactone polymerization.

Experimental

All manipulations with germanium and tin derivatives were performed under dry argon atmosphere using the standard Schlenk technique. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at room temperature (25 °C) on Bruker Avance 400 or

Table 1. Ring-opening polymerization of ε-caprolactone initiated by germylenes **8—10** and stannylenes **15—17**[a,b]

Run	Initiator	t/h	Conversion (%)	M_w	M_n	M_w/M_n
				g mol^{-1} [b]		
1	**8**	16	3	—	—	—
2	**9**	16	2	—	—	—
3	**10**	16	4	—	—	—
4	**15**	3	<1	—	—	—
5	**15**	4	3	—	—	—
6	**15**	5	32	—	—	—
7	**15**	7	92	11009	7019	1.57
8	**16**	1	3	—	—	—
9	**16**	3	38	—	—	—
10	**16**	6	93	—	—	—
11	**16**	10	>99	8418	5969	1.41
12	**17**	1	1	—	—	—
13	**17**	3	4	—	—	—
14	**17**	6	23	—	—	—
15[d]	**17**	16	93	9341	6788	1.38

[a] Bulk polymerization, 100 °C, [ε-caprolactone]$_0$: [tetrylene] : [BnOH]$_0$ = 300 : 1 : 1.
[b] The weight-average (M_w) and number-average (M_n) molecular weights of the synthesized polymers were determined by gel permeation chromatography taking into account the correction factor of 0.56.

Agilent 400 MR spectrometers operating at 400.13 (^{1}H), 100.61 (^{13}C), and 149.21 MHz (^{119}Sn); CDCl$_3$ and C$_6$D$_6$ were used as solvents and internal standards (residual protons of the deuterated solvents); chemical shifts are given with respect to Me$_4$Si or Me$_4$Sn. Elemental analysis was carried out in the Laboratory of Organic Microanalysis of the Department of Chemistry, M. V. Lomonosov Moscow State University.

The solvents were purified according to standard procedures. Diisopropylamine was distilled under argon atmosphere over calcium hydride (b.p. 84 °C, 760 mm Hg). 4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline,[31] 4,7-di(4-*tert*-butylphenoxy)-2,9-dimethyl-1,10-phenanthroline (**7**),[10] and M[N(SiMe$_3$)$_2$]$_2$ (M = Ge,[32] Sn[32]) were prepared by procedures described previously.

2,9-Dimethyl-4,7-di(4-methylphenoxy)-1,10-phenanthroline (6). 4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline (8.22 g, 0.030 mol), *p*-cresol (50.00 g, 0.330 mol), and KOH (7.00 g, 0.125 mol) were placed in a 250 mL Schlenk flask under argon atmosphere. The mixture was stirred for 48 h at 130 °C. The conversion was monitored by TLC (Silufol, EtOAc—methanol, 10 : 1). After completion of the reaction, the mixture was dissolved in CH$_2$Cl$_2$ (150 mL) and washed with a 2 *M* aqueous NaOH solution (500 mL). The organic phase was concentrated, and compound **6** was obtained as white powder. M.p. 68 °C. Yield 12.45 g (83%). ^{1}H NMR (CDCl$_3$), δ: 2.41 (s, 18 H, C(1)Me); 2.77 (s, 6 H, C(7)Me); 6.66 (s, 2 H, C(6)H); 7.10 (d, 4 H, C(3)H, J = 8.3 Hz); 7.27 (d, 4 H, C(2)H, J = 8.3 Hz); 8.28 (s, 2 H, C(10)H). ^{13}C NMR (CDCl$_3$), δ: 20.8 (C(7)Me); 26.3 (C(1)Me); 106.7, 118.36, 119.7, 120.9, 130.7, 135.2, 149.5, 152.1, 160.3, 162.1 (aromatic carbon atoms).

1,1′-((4,7-Bis(*p*-tolyloxy)-1,10-phenanthroline-2,9-diyl)bis-(methylene))dicyclohexanol (1). A 2.5 *M* n-butyllithium solution

in hexane (11 mL, 27.5 mmol) was added to a stirred solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous THF (15 mL) under argon atmosphere at −25 °C. The mixture was stirred at this temperature for 30 min. A solution of phenanthroline **6** (3.82 g, 9.1 mmol) in THF (70 mL) was added dropwise to the resulting lithium diisopropylamide under argon atmosphere at −80 °C. After 20 min, the temperature of the reaction mixture was increased to −20 °C, and the mixture was stirred at this temperature for 2 h. A solution of cyclohexanone (2.64 g, 22.7 mmol) in anhydrous THF (20 mL) was added dropwise to the resulting mixture at −20 °C, and the reaction mixture was stirred for 16 h. After completion of the reaction, the mixture was worked up with a saturated ammonium chloride solution (100 mL) and extracted with ethyl acetate (3×80 mL). The combined organic extracts were dried over Na$_2$SO$_4$, and volatile components were rotary evaporated. The yellow solid product was recrystalized from ethyl acetate. Compound **1** was obtained in a yield of 2.50 g (50%) as beige powder. ^{1}H NMR (CDCl$_3$), δ: 1.27—1.70 (m, 20 H, C(12)—(CH$_2$)$_5$—); 2.42 (s, 6 H, C(1)Me); 3.02 (s, 4 H, C(11)H$_2$); 6.63 (s, 2 H, C(6)H); 7.10 (d, 4 H, C(3)H, J = 8.1 Hz); 7.29 (d, 4 H, C(2)H, J = 8.1 Hz); 8.28 (s, 2 H, C(10)H). A signal of OH groups was absent in the spectrum. ^{13}C NMR (CDCl$_3$), δ: 20.9 (C(12)—(CH$_2$)$_5$—); 22.4 (C(1)Me); 25.9 (C(12)—CH$_2$)$_5$—); 38.0 (—(CH$_2$)$_5$—); 48.1 (C(12)OH); 71.6 (C(11)H$_2$); 108.1, 118.7, 120.0, 120.7, 126.3, 130.8, 135.3, 152.1, 161.4, 162.4 (aromatic carbon atoms). Found (%): C, 77.70; H, 7.09; N, 4.63. C$_{40}$H$_{44}$N$_2$O$_4$. Calculated (%): C, 77.89; H, 7.19; N, 4.54.

1,1′-(4,7-Bis(*p*-tolyloxy)-1,10-phenanthroline-2,9-diyl)bis-(2-methylpropan-2-ol) (2). A 2.5 *M* n-butyllithium solution in hexane (11 mL, 27.5 mmol) was added to a stirred solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous THF (15 mL) under argon atmosphere at −25 °C. The mixture was stirred at this temperature for 30 min. A solution of phenanthroline **6** (3.82 g, 9.1 mmol) in THF (70 mL) was added dropwise to the resulting lithium diisopropylamide under argon atmosphere at −80 °C. After 20 min, the temperature of the reaction mixture was increased to −20 °C, and the mixture was stirred at this temperature for 2 h. A solution of acetone (1.32 g, 22.7 mmol) in anhydrous THF (20 mL) was added dropwise to the resulting mixture at −20 °C, and the reaction mixture was stirred for 16 h. After completion of the reaction, the mixture was worked up with a saturated ammonium chloride solution (100 mL) and extracted with ethyl acetate (3×80 mL). The combined organic extracts were dried over Na$_2$SO$_4$, and volatile components were rotary evaporated. The yellow solid product was recrystallized from ethyl acetate. Compound **2** was obtained in a yield of 1.90 g (45%) as yellowish powder. ^{1}H NMR (CDCl$_3$), δ: 1.23 (s, 12 H, C(12)(Me)$_2$); 2.41 (s, 6 H, C(1)Me); 3.01 (s, 4 H, C(11)H$_2$); 6.62 (s, 2 H, C(6)H); 7.11 (d, 4 H, C(3)H, J = 8.2 Hz); 7.29 (d, 4 H, C(2)H, J = 8.2 Hz); 8.31 (s, 2 H, C(10)H). A signal of OH groups was absent in the spectrum. ^{13}C NMR (CDCl$_3$), δ: 20.9 (C(12)(Me)$_2$); 29.6 (C(1)Me); 49.6 (C(12)OH); 70.6 (C(11)H$_2$); 107.8, 118.7, 119.9, 120.7, 120.9, 130.7, 130.9, 139.0, 145.6, 161.8 (aromatic carbon atoms). Found (%): C, 75.73; H, 6.60; N, 5.35. C$_{34}$H$_{36}$N$_2$O$_4$. Calculated (%): C, 76.09; H, 6.76; N, 5.22.

1,1′-[(4,7-Bis(*p*-tolyloxy)-1,10-phenanthroline-2,9-diyl)-bis(methylene)]diadamantanol (3). A 2.5 *M* n-butyllithium solution in hexane (11 mL, 27.5 mmol) was added to a stirred solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous THF (15 mL) under argon atmosphere at −25 °C. The reaction mixture was stirred at this temperature for 30 min. A solution of phenanthroline **6** (3.82 g, 9.1 mmol) in THF (70 mL) was added dropwise

to the resulting lithium diisopropylamide under argon atmosphere at $-80\ °C$. After 20 min, the temperature of the reaction mixture was increased to $-20\ °C$, and the mixture was stirred at this temperature for 2 h. A solution of 2-adamantanone (3.41 g, 22.7 mmol) in anhydrous THF (20 mL) was added dropwise to the resulting mixture at $-20\ °C$. The mixture was stirred for 16 h. After completion of the reaction, the mixture was worked up with a saturated ammonium chloride solution (100 mL) and extracted with ethyl acetate (3×80 mL). The combined organic extracts were dried over Na_2SO_4, and volatile components were rotary evaporated. The residue was purified by silica gel column chromatography (elution with EtOAc—petroleum ether (1 : 3); R_f(**3**) 0.1, R_f(2-adamantanone) 0.7). The fractions were concentrated, and compound **3** was obtained in a yield of 2.40 g (47%) as orange powder. ¹H NMR ($CDCl_3$), δ: 1.65 (s, 6 H, C(1)M̲e̲); 1.63—2.08 (m, 22 H, C(12) 2,2-adamantylene); 2.42 (s, 4 H, 2,2-adamantylene); 3.27 (s, 4 H, C(11)H₂); 6.68 (s, 2 H, C(6)H̲); 7.09 (d, 4 H, C(3)H̲, $J = 8.1$ Hz); 7.29 (d, 4 H, C(2)H̲, $J = 8.1$ Hz); 8.28 (s, 2 H, C(10)H̲). A signal of OH groups was absent in the spectrum. ¹³C NMR ($CDCl_3$), δ: 30.3 (C(1)M̲e̲); 27.4, 27.5, 30.3, 32.8, 34.6, 36.3, 37.3, 38.6 (2,2-adamantylene); 46.9 (C̲(12)OH); 75.4 (C̲(11)H₂); 116.6, 118.6, 118.7, 120.6, 130.8, 132.7, 134.3, 155.1, 159.0, 161.5 (aromatic carbon atoms). Found (%): C, 80.25; H, 7.39; N, 3.78. $C_{48}H_{52}N_2O_4$. Calculated (%): C, 79.97; H, 7.27; N, 3.89.

1,1′-[(4,7-Di(4-*tert*-butylphenoxy)-1,10-phenanthroline-2,9-diyl)bis(methylene)]dicyclohexanol (4). A 2.5 *M* n-butyllithium solution in hexane (11 mL, 27.5 mmol) was added to a stirred solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous THF (15 mL) under argon atmosphere at $-25\ °C$. The mixture was stirred at this temperature for 30 min. A solution of phenanthroline **7** (4.58 g, 9.1 mmol) in THF (70 mL) was added dropwise to the resulting lithium diisopropylamide under argon atmosphere at $-80\ °C$. After 20 min, the temperature of the reaction mixture was increased to $-20\ °C$, and the mixture was stirred at this temperature for 2 h. A solution of cyclohexanone (2.64 g, 22.7 mmol) in anhydrous THF (20 mL) was added dropwise to the resulting mixture at $-20\ °C$. The mixture was stirred for 16 h. After completion of the reaction, the mixture was worked up with a saturated ammonium chloride solution (100 mL) and extracted with ethyl acetate ($3\frac{1}{2}80$ mL). The combined organic extracts were dried over Na_2SO_4, and volatile components were rotary evaporated. The yellow solid product was recrystallized from ethyl acetate. Compound **4** was obtained in a yield of 2.70 g (49%) as yellowish powder. ¹H NMR ($CDCl_3$), δ: 1.25—1.74 (m, 20 H, C(12)—(CH̲₂)₅—); 1.38 (s, 18 H, C(1)CM̲e₃); 3.05 (s, 4 H, C(11)H₂); 6.69 (s, 2 H, C(6)H̲); 7.13 (d, 4 H, C(3)H̲, $J = 8.8$ Hz); 7.49 (d, 4 H, C(2)H̲, $J = 8.1$ Hz); 8.27 (s, 2 H, C(10)H̲). A signal of OH groups was absent in the spectrum. ¹³C NMR ($CDCl_3$), δ: 22.4 (C(12)—(C̲H₂)₅—); 26.0 (C(12)C̲H₂)₅—); 31.5 (C(1)CM̲e₃); 34.6 (C(1)C̲Me₃); 38.0 (—(C̲H₂)₅—); 48.2 (C̲(12)OH); 71.6 (C̲(11)H₂); 108.3, 118.7, 120.1, 120.1, 127.2, 145.8, 148.5, 152.1, 161.5, 162.1 (aromatic carbon atoms). Found (%): C, 78.80; H, 8.00; N, 3.99. $C_{46}H_{56}N_2O_4$. Calculated (%): C, 78.82; H, 8.05; N, 4.00.

1,1′-[4,7-Bis(4-*tert*-butylphenoxy)-1,10-phenanthroline-2,9-diyl]bis(2-methylpropan-2-ol) (5). A 2.5 *M* n-butyllithium solution in hexane (11 mL, 27.5 mmol) was added to a stirred solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous THF (15 mL) under argon atmosphere at $-25\ °C$. The mixture was stirred at this temperature for 30 min. Then a solution of phenanthroline

7 (4.58 g, 9.1 mmol) in THF (70 mL) was added dropwise to the resulting lithium diisopropylamide under argon atmosphere at $-80\ °C$. After 20 min, the temperature of the reaction mixture was increased to $-20\ °C$, and the mixture was stirred at this temperature for 2 h. A solution of acetone (1.32 g, 22.7 mmol) in anhydrous THF (20 mL) was added dropwise to the resulting mixture at $-20\ °C$. The mixture was stirred for 16 h. After completion of the reaction, the mixture was worked up with a saturated ammonium chloride solution (100 mL) and extracted with ethyl acetate (3×80 mL). The combined extracts were dried over Na_2SO_4, and volatile components were rotary evaporated. The yellow solid product was recrystallized from a methanol—ethyl acetate mixture (1 : 5). Compound **5** was obtained in a yield of 2.00 g (40%) as yellowish powder. ¹H NMR ($CDCl_3$), δ: 1.38 (s, 18 H, C(1)CM̲e₃); 1.47 (s, 6 H, C(12)M̲e); 1.49 (s, 6 H, C(12)M̲e); 3.03 (s, 4 H, C(11)H₂); 6.67 (s, 2 H, C(6)H̲); 7.14 (d, 4 H, C(3)H̲, $J = 8.6$ Hz); 7.50 (d, 4 H, C(2)H̲, $J = 8.6$ Hz); 8.29 (s, 2 H, C(10)H̲). A signal of OH groups was absent in the spectrum. ¹³C NMR ($CDCl_3$), δ: 31.4 (C(1)CM̲e₃); 36.6 (C(1)C̲Me₃); 46.0 (s, 4 H, C(12)M̲e₂); 53.2 (C̲(12)OH); 72.6 (C̲(11)H₂); 120.3, 120.6, 128.1, 129.0, 131.2, 136.0, 141.5, 152.9, 153.6, 164.1 (aromatic carbon atoms). Found (%): C, 77.58; H, 7.85; N, 4.40. $C_{40}H_{48}N_2O_4$. Calculated (%): C, 77.39; H, 7.79; N, 4.51.

Germylene 8. A solution of ligand **1** (0.25 g 0.70 mmol) in toluene (10 mL) was added dropwise to a stirred solution of germanium(ii) bis(trimethylsilyl)amide (0.27 g, 0.70 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After stirring for 30 min, the solution turned red; after a few hours, the color of the solution changed to violet. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The solid residue was washed with hexane. Compound **8** was obtained in a yield of 0.31 g (62%) as grayish powder. ¹H NMR ($CDCl_3$), δ: 1.25—1.57 (m, 20 H, C(12)—(CH̲₂)₅—); 2.42 (s, 6 H, C(1)M̲e); 3.03 (s, 4 H, C(11)H₂); 6.74 (s, 2 H, C(6)H̲); 7.03 (d, 4 H, C(3)H̲, $J = 7.6$ Hz); 7.12 (d, 4 H, C(2)H̲, $J = 7.6$ Hz); 8.28 (s, 2 H, C(10)H̲). ¹³C NMR ($CDCl_3$), δ: 20.9 (C(12)—(C̲H₂)₅—); 35.9 (C(1)M̲e); 38.0 (C(12)—C̲H₂)₅—); 50.3 (—(C̲H₂)₅—); 55.6 (C̲(12)OGe); 72.5 (C̲(11)H₂); 107.6, 120.2, 120.7, 129.9, 138.3, 158.8, 161.2 (aromatic carbon atoms). Found (%): C, 69.99; H, 6.23; N, 4.03. $C_{40}H_{42}GeN_2O_4$. Calculated (%): C, 69.89; H, 6.16; N, 4.08.

Germylene 9. A solution of ligand **2** (0.41 g, 0.70 mmol) in toluene (10 mL) was added dropwise to a stirred solution of germanium(ii) bis(trimethylsilyl)amide (0.27 g, 0.70 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After stirring for 30 min, the solution turned red; after a few hours, the color of the solution changed to violet. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The solid residue was washed with hexane. Compound **9** was obtained in a yield of 0.20 g (50%) as gray-green powder. ¹H NMR (C_6D_6), δ: 1.20 (s, 12 H, C(12)(Me)₂); 1.23 (s, 6 H, C(1)M̲e); 2.41 (s, 4 H, C(11)H₂); 6.61 (s, 2 H, C(6)H̲); 6.92 (d, 4 H, C(3)H̲, $J = 8.7$ Hz); 7.25 (d, 4 H, C(2)H̲, $J = 8.6$ Hz); 8.50 (s, 2 H, C(10)H̲). ¹³C NMR (C_6D_6), δ: 20.5 (C(12)(M̲e)₂); 20.8 (C(1)M̲e); 29.6 (C̲(12)OGe); 74.7 (C̲(11)H₂); 106.7, 118.3, 119.7, 120.7, 120.9, 129.8, 131.3, 152.1, 160.3 (aromatic carbon atoms). Found (%): C, 67.34; H, 5.72; N, 4.59. $C_{34}H_{34}GeN_2O_4$. Calculated (%): C, 67.24; H, 5.64; N, 4.61.

Germylene 10. A solution of ligand **3** (0.50 g, 0.70 mmol) in toluene (10 mL) was added dropwise to a stirred solution of

germanium(II) bis(trimethylsilyl)amide (0.27 g, 0.70 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After stirring for 30 min, the solution turned red; after a few hours, the color of the solution changed to violet. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The solid residue was washed with hexane. Compound **10** was obtained in a yield of 0.36 g (65%) as gray powder. ^{1}H NMR (CDCl$_3$), δ: 1.64 (s, 6 H, C(1)$\underline{\text{Me}}$); 1.60—1.88 (m, 22 H, C(12) 2,2-adamantylene); 2.40 (s, 4 H, 2,2-adamantylene); 3.25 (s, 4 H, C(11)H$_2$); 6.64 (s, 2 H, C(6)$\underline{\text{H}}$); 7.07 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 7.8 Hz); 7.27 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 7.8 Hz); 8.25 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$), δ: 20.5, 22.8, 23.7, 27.5, 28.9, 29.6, 30.3, 32.8, 34.7 (2,2-adamantylene); 37.3 (C(1)$\underline{\text{Me}}$); 38.7 ($\underline{\text{C}}$(12)OGe); 68.1 ($\underline{\text{C}}$(11)H$_2$); 108.3, 119.8, 120.5, 128.7, 129.8, 130.8, 132.4, 144.6, 161.5, 162.1 (aromatic carbon atoms). Found (%): C, 72.90; H, 6.42; N, 3.50. C$_{48}$H$_{50}$GeN$_2$O$_4$. Calculated (%): C, 72.83; H, 6.37; N, 3.54.

Germylene 11. A solution of ligand **4** (0.49 g, 0.70 mmol) in toluene (10 mL) was added dropwise to a stirred solution of germanium(II) bis(trimethylsilyl)amide (0.27 g, 0.70 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After stirring for 30 min, the solution turned red; after a few hours, the color of the solution changed to dark-blue. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The solid residue was washed with hexane. Compound **11** was obtained in a yield of 0.32 g (60%) as gray powder. ^{1}H NMR (C$_6$D$_6$), δ: 1.20 (s, 18 H, C(1)C$\underline{\text{Me}}_3$); 1.22—1.45 (m, 20 H, C(12)—(C$\underline{\text{H}}_2$)$_5$); 2.70 (s, 4 H, C(11)H$_2$); 6.65 (s, 2 H, C(6)$\underline{\text{H}}$); 7.02 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 8.8 Hz); 7.27 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 8.1 Hz); 8.47 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (C$_6$D$_6$), δ: 21.8 (C(12)—($\underline{\text{C}}$H$_2$)$_5$—); 22.9 (C(12)$\underline{\text{C}}$H$_2$)$_5$—); 31.8 (C(1)C$\underline{\text{Me}}_3$); 34.9 (C(1)$\underline{\text{C}}$Me$_3$); 38.8 (—($\underline{\text{C}}$H$_2$)$_5$—); 49.8 ($\underline{\text{C}}$(12)OGe); 71.60 ($\underline{\text{C}}$(11)H$_2$); 109.0, 119.4, 121.2, 126.0, 129.7, 138.2, 147.0, 149.1, 153.1, 162.9 (aromatic carbon atoms). Found (%): C, 71.44; H, 7.19; N, 3.65. C$_{46}$H$_{54}$GeN$_2$O$_4$. Calculated (%): C, 71.61; H, 7.05; N, 3.63.

Germylene 12. A solution of ligand **5** (0.43 g, 0.70 mmol) in toluene (10 mL) was added dropwise to a stirred solution of germanium(II) bis(trimethylsilyl)amide (0.27 g, 0.70 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After stirring for 30 min, the solution turned red; after a few hours, the color of the solution changed to violet. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The solid residue was washed with hexane. Compound **12** was obtained in a yield of 0.24 g (50%) as gray-green powder. ^{1}H NMR (C$_6$D$_6$), δ: 1.20 (s, 12 H, C(12)$\underline{\text{Me}}_2$); 1.23 (s, 18 H, C(1)C$\underline{\text{Me}}_3$); 2.47 (s, 4 H, C(11)H$_2$); 6.61 (s, 2 H, C(6)$\underline{\text{H}}$); 6.92 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 8.7 Hz); 7.25 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 8.6 Hz); 8.50 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (C$_6$D$_6$), δ: 31.8 (C(1)C$\underline{\text{Me}}_3$); 32.0 (C(1)$\underline{\text{C}}$Me$_3$); 38.0 (s, 4 H, C(12)$\underline{\text{Me}}_2$); 43.1 ($\underline{\text{C}}$(12)OGe); 54.7 ($\underline{\text{C}}$(11)H$_2$); 105.6, 112.9, 120.2, 121.2, 126.0, 127.0, 127.8, 129.7, 148.7, 167.2 (aromatic carbon atoms). Found (%): C, 69.95; H, 6.88; N, 3.99. C$_{40}$H$_{46}$GeN$_2$O$_4$. Calculated (%): C, 69.48; H, 6.71; N, 4.05.

Stannylene 13. A solution of ligand **1** (0.29 g, 0.48 mmol) in toluene (7 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.25 g, 0.48 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After the addition of ligand **1**, the mixture turned dark-brown. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The reaction product was

recrystallized from a toluene—hexane mixture (4 : 1). Compound **13** was obtained in a yield of 0.23 g (51%) as gray-brown powder. ^{1}H NMR (CDCl$_3$), δ: 1.22—1.59 (m, 20 H, C(12)—(C$\underline{\text{H}}_2$)$_5$—); 2.40 (s, 6 H, C(1)$\underline{\text{Me}}$); 3.00 (s, 4 H, C(11)H$_2$); 6.61 (s, 2 H, C(6)$\underline{\text{H}}$); 7.07 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 7.1 Hz); 7.25 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 7.1 Hz); 8.22 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$), δ: 20.9 (C(12)—($\underline{\text{C}}$H$_2$)$_5$—); 22.5 (C(1)$\underline{\text{Me}}$); 29.9 (C(12)—$\underline{\text{C}}$H$_2$)$_5$—); 38.2 (—($\underline{\text{C}}$H$_2$)$_5$—); 48.0 ($\underline{\text{C}}$(12)OSn); 71.5 ($\underline{\text{C}}$(11)H$_2$); 107.8, 118.1, 118.8, 128.2, 120.7, 129.0, 130.8, 146.4, 158.6, 162.3 (aromatic carbon atoms). Found (%): C, 64.98; H, 5.63; N, 3.99. C$_{40}$H$_{42}$SnN$_2$O$_4$. Calculated (%): C, 65.50; H, 5.77; N, 3.82.

Stannylene 14. A solution of ligand **2** (0.37 g, 0.61 mmol) in toluene (7 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.27 g, 0.61 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After the addition of ligand **2**, the mixture turned dark-brown. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The reaction product was recrystallized from a toluene—hexane mixture (4 : 1). Compound **14** was obtained in a yield of 0.22 g (52%) as gray-brown powder. ^{1}H NMR (CDCl$_3$), δ: 1.21 (s, 12 H, C(12)(Me)$_2$); 2.41 (s, 6 H, C(1)$\underline{\text{Me}}$); 2.99 (s, 4 H, C(11)H$_2$); 6.63 (s, 2 H, C(6)$\underline{\text{H}}$); 7.08 (d, 4 H, C(3)$\underline{\text{H}}$); 7.25 (d, 4 H, C(2)$\underline{\text{H}}$); 8.25 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (C$_6$D$_6$), δ: 20.9 (C(12)($\underline{\text{Me}}$)$_2$); 29.6 (C(1)$\underline{\text{Me}}$); 49.6 ($\underline{\text{C}}$(12)OSn); 70.6 ($\underline{\text{C}}$(11)H$_2$); 107.8 118.7, 119.9, 120.7, 120.9, 130.7, 130.9, 139.0, 145.6, 161.8 (aromatic carbon atoms). Found (%): C, 63.18; H, 5.35; N, 4.10. C$_{34}$H$_{34}$SnN$_2$O$_4$. Calculated (%): C, 62.50; H, 5.25; N, 4.29.

Stannylene 15. A solution of ligand **3** (0.49 g, 0.68 mmol) in toluene (7 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.30 g, 0.68 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After the addition of ligand **3**, the mixture turned dark-red. The reaction mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The reaction product was recrystallized from a toluene—hexane mixture (4 : 1). Compound **15** was obtained in a yield of 0.30 g (51%) as reddish-gray powder. ^{1}H NMR (CDCl$_3$), δ: 1.66—2.09 (m, 22 H, C(12) 2,2-adamantylene); 2.43 (s, 6 H, C(1)$\underline{\text{Me}}$); 2.57 (s, 2 H, C(11)H$_2$); 2.81 (s, 2 H, C(11)H$_2$); 6.70 (s, 2 H, C(6)$\underline{\text{H}}$); 7.08 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 7.8 Hz); 7.31 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 7.8 Hz); 8.24 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$), δ: 27.9, 33.1, 34.2, 34.8, 35.2, 38.6, 39.2, 43.6 (2,2-adamantylene); 36.3 (C(1)$\underline{\text{Me}}$); 45.9 ($\underline{\text{C}}$(12)OSn); 68.1 ($\underline{\text{C}}$(11)H$_2$); 108.9, 118.4, 119.6, 120.5, 131.0, 135.8, 142.78, 151.7, 161.9, 162.9 (aromatic carbon atoms). ^{119}Sn NMR (C$_6$D$_6$), δ: −365.2. Found (%): C, 69.50; H, 6.45; N, 3.58. C$_{48}$H$_{50}$SnN$_2$O$_4$. Calculated (%): C, 68.83; H, 6.02; N, 3.34.

Stannylene 16. A solution of ligand **4** (0.40 g, 0.57 mmol) in toluene (7 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.25 g, 0.57 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After the addition of ligand **4**, the mixture turned dark-green. The mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The reaction product was recrystallized from a toluene—hexane mixture (4 : 1). Compound **16** was obtained in a yield of 0.20 g (50%) as gray powder. ^{1}H NMR (CDCl$_3$), δ: 1.38 (s, 18 H, C(1)C$\underline{\text{Me}}_3$); 1.32—1.60 (m, 20 H, C(12)—(C$\underline{\text{H}}_2$)$_5$—); 3.05 (s, 4 H, C(11)H$_2$); 6.70 (s, 2 H, C(6)$\underline{\text{H}}$); 7.13 (d, 4 H, C(3)$\underline{\text{H}}$, *J* = 8.6 Hz); 7.49 (d, 4 H, C(2)$\underline{\text{H}}$, *J* = 8.6 Hz); 8.26 (s, 2 H, C(10)$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$), δ: 22.4 (C(12)—(C$\underline{\text{H}}_2$)$_5$—); 26.0 (C(12)$\underline{\text{C}}$H$_2$)$_5$—); 31.5 (C(1)C$\underline{\text{Me}}_3$); 34.6

(C(1)$\underline{C}$Me$_3$); 38.1 (—($\underline{C}$H$_2$)$_5$—); 48.3 ($\underline{C}$(12)OSn); 71.5 ($\underline{C}$(11)H$_2$); 108.4, 118.7, 120.1, 120.2, 127.1, 145.9, 148.5, 152.2, 161.5, 162.1 (aromatic carbon atoms). ^{119}Sn NMR (CDCl$_3$), δ: −320.1. Found (%): C, 67.48; H, 6.85; N, 3.54. C$_{46}$H$_{54}$GeN$_2$O$_4$. Calculated (%): C, 67.57; H, 6.66; N, 3.43.

Stannylene 17. A solution of ligand **5** (0.30 g, 0.61 mmol) in toluene (7 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.27 g, 0.61 mmol) in toluene (10 mL) under argon atmosphere at room temperature. After the addition of ligand **5**, the mixture turned brown. The mixture was stirred for 24 h at room temperature, and volatile components were removed under high vacuum. The reaction product was recrystallized from a toluene—hexane mixture (4 : 1). Compound **17** was obtained in a yield of 0.20 g (60%) as gray-brown powder. ^{1}H NMR (CDCl$_3$), δ: 1.24 (s, 12 H, C(12)$\underline{Me}_2$); 1.38 (s, 18 H, C(1)C$\underline{Me}_3$); 3.03 (s, 4 H, C(11)$\underline{H}_2$); 6.71 (s, 2 H, C(6)$\underline{H}$); 7.08 (d, 4 H, C(3)$\underline{H}$, J = 8.9 Hz); 7.50 (d, 4 H, C(2)$\underline{H}$, J = 8.9 Hz); 8.24 (s, 2 H, C(10)$\underline{H}$). ^{13}C NMR (CDCl$_3$), δ: 29.7 (C(1)C$\underline{Me}_3$); 31.4 (C(1)$\underline{C}$Me$_3$); 34.6 (s, 4 H, C(12)$\underline{Me}_2$); 48.8 ($\underline{C}$(12)OSn); 70.5 ($\underline{C}$(11)H$_2$); 108.0, 118.0, 118.7, 120.3, 127.2, 128.2, 129.0, 148.6, 151.9, 161.5 (aromatic carbon atoms). ^{119}Sn NMR (C$_6$D$_6$), δ: −349.6. Found (%): C, 67.04; H, 6.45; N, 3.99. C$_{40}$H$_{46}$SnN$_2$O$_4$. Calculated (%): C, 65.14; H, 6.29; N, 3.80.

X-ray diffraction study of compound **4** was performed on a Bruker SMART APEX II automated diffractometer at 150 K using Mo$K\alpha$ radiation (λ = 0.71073 Å, graphite monochromator). Crystals of compound **4** (C$_{48}$H$_{58}$Cl$_6$N$_2$O$_4$, M = 939.66) are monoclinic, space group $C2/c$, a = 27.631(7) Å, b = 10.274(2) Å, c = 18.866(4) Å, β = 117.313(4)°, V = 4758.5(19) Å^3, Z = 4, d_{calc} = 1.312 g cm^{-3}, μ(Mo$K\alpha$) = 0.406 mm^{-1}, $F(000)$ = 1976. The intensities of 24520 reflections (5757 unique reflections, R_{int} = 0.0309) were measured using the ω-scan technique with a step of 0.5° in the angle range 2.15 < θ < 28.00° (−36 ≤ h ≤ 36, −13 ≤ k ≤ 13, −24 ≤ l ≤ 24). The absorption correction was applied based on intensities of equivalent reflections.[33] The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for all nonhydrogen atoms (Shelxtl).[34] The positions of all hydrogen atoms were found in difference Fourier maps and refined isotropically. The refinement converged to R_1 = 0.0374 based on 4539 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0982 based on a total data set using 387 refinement parameters; GoF = 1.038, ρ_{min}/ρ_{max} = −0.417/0.398 e Å^3. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 1878769). The X-ray diffraction study was performed using equipment of the Shared Facility Center of the N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

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